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# An Evaluation of Carbon Steel Corrosion under Stagnant Seawater Conditions

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Corrosion of 1020 carbon steel coupons in natural seawater over a 1-year period was more aggressive under strictly anaerobic stagnant conditions than under aerobic stagnant conditions as measured by weight loss and instantaneous corrosion rate (polarization resistance). Under oxygenated conditions, a two-tiered oxide layer of lepidocrocite/goethite formed. The inner layer was extremely tenacious and resistant to acid cleaning. Under anaerobic conditions, the corrosion product was initially a non-tenacious sulphur-rich corrosion product, mackinawite, with enmeshed bacteria. As more sulphide was produced the mackinawite was transformed to pyrrhotite. In both aerobic and anaerobic exposures, corrosion was more aggressive on horizontally oriented coupons compared to vertically oriented samples.

*Keywords*: seawater; aerobic; anaerobic; sulphate-reducing bacteria

## INTRODUCTION

Hamilton (2003) recently proposed a model for corrosion of carbon steel due to sulphate-reducing bacteria (SRB) in which sulphate, an intermediate electron acceptor, is reduced to sulphide. In his model, sulphide reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. Hamilton's theory provides insight into electron transfer reactions within a biofilm containing both aerobic and anaerobic niches. Consistent with that model, most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium (Hamilton & Maxwell, 1986; Hamilton & Sanders, 1986). Key West, FL, seawater typically contains 2 g $l^{-1}$ sulphate and 5–7 mg $l^{-1}$ dissolved $O_2$. Lee *et al.* (1993a; 1993b) and Hardy and Bown (1984) demonstrated that the most aggressive corrosion due to SRB occurs when carbon steel is exposed to alternating oxygenated/anaerobic conditions. Hardy and Bown (1984) conducted experiments in an artificial seawater medium to which they added 1.0 g $l^{-1}$ $NH_4Cl$, 0.1 g $l^{-1}$ $KH_2PO_4$, 0.1 g $l^{-1}$ $Fe(NH_4)_2(SO_4)_2.6H_2O$, 0.4 g $l^{-1}$ Tris[tris-(hydroxy methyl) amino methane], 4.5 ml 60% sodium DL lactate, 0.5 g $l^{-1}$ yeast extract, 1.0 g $l^{-1}$ ascorbic acid in 750 ml synthetic seawater and 250 ml distilled water. The experiments were conducted using a single marine isolate, *Desulfovibrio* sp. Corrosion rates of mild steel foils (25 $\mu$m thick, undefined surface area and finish) were determined by weight loss measurements and by electrical resistance probe measurements. In their experiments corrosion rates in anaerobic media were low (1.45 mg $dm^{-2}$ $d^{-1}$). Exposure to air caused corrosion rates to increase (129 mg $dm^{-2}$ $d^{-1}$) and localized corrosion was observed. The experiments of Lee *et al.* (1993a; 1993b) were conducted with an artificial seawater medium containing 10 mg $l^{-1}$ glucose, 25 mg $l^{-1}$ sodium lactate, 25 mg $l^{-1}$ sodium acetate, 10 mg $l^{-1}$ yeast extract, 10 mg $l^{-1}$ $NH_4Cl$ and 2 mg $l^{-1}$ $Na_2HPO_4$ inoculated with *Pseudomonas aeruginosa*, *Klebsiella pneumonia* and *Desulfovibrio desulphuricans*. Lee *et al.* (1993a; 1993b) used electrochemical techniques to evaluate corrosion of 1018 carbon steel (polished to 600 grit) and concluded that the corrosion rate under

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totally anaerobic conditions was negligible compared to that under aerobic conditions. Both sets of experiments were used in the formulation of Hamilton's unifying theory of microbiologically influenced corrosion (MIC) with oxygen as the terminal electron acceptor. However, it is not clear that the results from Lee *et al.* (1993a; 1993b) and Hardy and Bown (1984) can be directly transitioned to exposures of carbon steel to natural seawater with no additives and a natural microflora. Furthermore, Hamilton's theory (2003) does not address corrosion rates in oxygenated and deoxygenated waters. The details of carbon steel corrosion in stagnant natural seawater are significant because of proposals to remove oxygen from seawater ballast as a corrosion control procedure for tanks that are not protected by coatings or cathodic protection (Matsuda *et al.*, 1999; Tamburri *et al.*, 2002). In this paper laboratory experiments are described which were designed to test the hypothesis that oxygen is required for aggressive corrosion of carbon steel exposed to natural seawater. Uncoated carbon steel was maintained under the following stagnant conditions: i) natural seawater open to air and ii) anaerobic natural seawater stripped of oxygen.

## MATERIALS AND METHODS

Identical chambers were built to expose 1020 carbon steel and natural seawater to the defined operating conditions (Figure 1). Cylindrical chambers (35.5 cm diameter and 27.9 cm high) were constructed from heavy gauge, chemical resistant, opaque polyethylene. Corrosion coupons were descaled, non-polished 1020 carbon steel (Table I), 1.5 cm diameter × 0.16 cm thick (Metals Samples®, Munford, AL) with an as-mill finish. Individual insulated wires were attached to the back of each sample and held in place using conductive silver adhesive (Electron Microscopy Sciences®, Fort Washington, PA) and carbon tape. The exposure side of the coupon was coated with vacuum grease and centred face down inside a plastic mount (3.175 cm diameter × 2.54 cm high). Samples were mounted in Epothin® epoxy

TABLE I The chemical composition of carbon steel 1020

| AISI-SAE designation | C | Mn | P max | S max | Fe |
|---|---|---|---|---|---|
| 1020 | 0.17–0.24 | 0.25–0.60 | 0.04 | 0.05 | remainder |

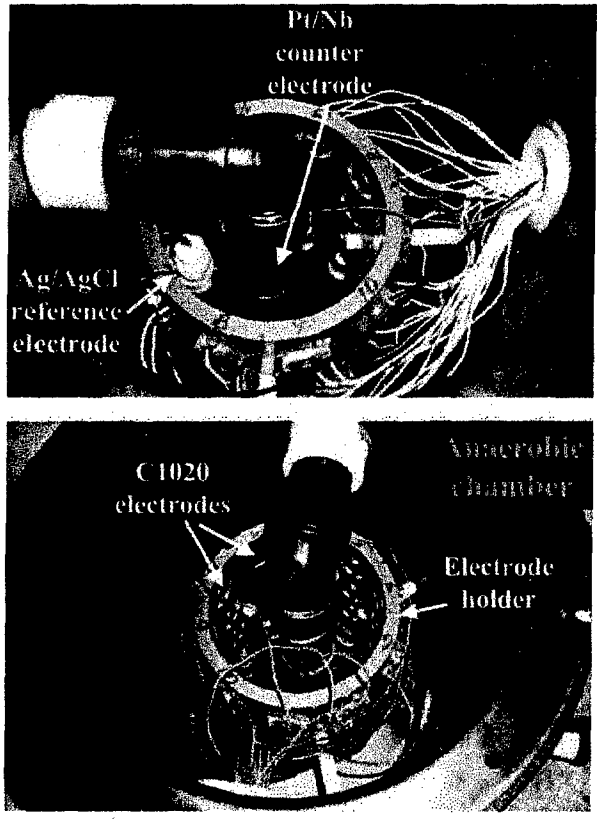


FIGURE 1 Heavy gauge plastic experimental chambers each containing an Ag/AgCl reference electrode, a Pt/Nb mesh counter, a cylindrical electrode holder and 36 individually addressable C1020 electrodes (27 vertically orientated, 9 horizontally orientated).

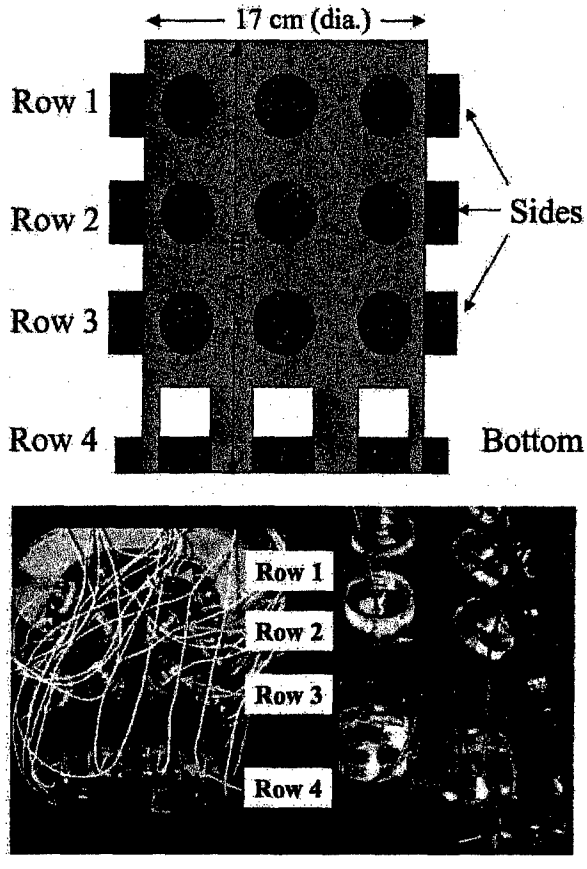


FIGURE 2 Electrode holder and individual electrodes orientated both horizontally (bottom) and vertically (sides).

(Buehler, Lake Bluff, IL) with the wire connection exposed to the epoxy. Vacuum grease prevented intrusion of epoxy between the sample face and the bottom of the mount and allowed the as-mill finish to be preserved. Epoxy-mounted carbon steel coupons were oriented in rows both vertically (27 samples) and horizontally (9 samples) in each chamber to simulate tank sidewalls and bottoms, respectively, for a total of 36 samples (Figure 2). A heavy gauge plastic cylinder (17 cm diameter × 23 cm high) held the electrodes in place with the vertically oriented samples positioned inwards and the horizontally oriented samples positioned upwards. Prior to seawater exposure, coupons were rinsed in acetone, ethanol and distilled water and dried with nitrogen gas to removed vacuum grease and residual surface debris. A Ag/AgCl electrode and a platinum/niobium mesh were used as reference and counter electrodes, respectively (Figure 1). Exposure chambers were filled with natural seawater collected at the Naval Research Laboratory (NRL) Corrosion Facility, Key West, FL. Natural Key West, FL seawater was deoxygenated using a premixed inert gas containing $CO_2$.

Chambers containing stagnant seawater were sealed and transported to NRL, Stennis Space Center, MS. The chamber filled with natural, oxygenated seawater was open to air *via* a 1-inch tube in the chamber cover. The chamber filled with anaerobic water was maintained in an anaerobic hood with an atmosphere of 5% $CO_2$, 10% $H_2$ and the balance $N_2$.

Water samples from the midsections of each stagnant chamber were collected monthly using a sterile 20 ml pipette. The following parameters were measured using standard techniques (Acculab® Incorporated, Marrero, LA): dissolved oxygen, ammonia nitrogen, nitrate and nitrite, bulk pH, sulphate concentrations and turbidity. Sulphide concentrations were determined in triplicate using the methylene blue method 228 C (Standard Methods, 1971) and Hach® Odyssey DR2500 spectrophotometer/software. A sterile 5 ml syringe was used to remove 4 ml from the 20 ml water sample. One ml was used to inoculate serial dilutions ($10^5$) of each of the following seawater media (Dixie Testing and Products Incorporated®, Houston, TX): phenol red dextrose broth (Difco®), Postgate medium B, nutrient broth (Difco®) and thioglycollate medium (Difco®) used to determine most probable numbers of acid-producing bacteria (APB), SRB, general heterotrophic aerobes, and anaerobes, respectively. Dilutions were incubated for 28 d at room temperature.

Four coupons (1 horizontally and 3 vertically orientated) were removed monthly. Coupons were fixed in cacodylate buffered 4% glutaraldehyde in seawater, rinsed in distilled water and examined using environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) to characterize corrosion morphology, biofilm structure and corrosion product composition (Pope *et al.*, 2000). After ESEM evaluation, coupons were cleaned with an acid solution (ASTM, 1994), weighed (Denver Instrument Company, Model TC-104, precision + / − 0.1 mg) and re-examined with ESEM. Some coupons required additional treatment in a boiling caustic solution containing 20 g NaOH and 2 g Zn in 100 ml distilled water. The open-circuit potential ($E_{corr}$) was monitored continuously using an Agilent® HP34970A data logger and linear polarization resistance (LPR) was performed on each sample every 1 – 3 months. LPR was used to determine the polarization resistance ($R_p$) of each electrode. The inverse ($1/R_p$) is the instantaneous corrosion rate given in ($ohms^{-1}$). Acquisition time for $R_p$ is $< 1$ min. Dissolved oxygen (DO) in each container was monitored continuously using a dissolved oxygen electrode (OxyGuard® DO Probe, Port Moody, British Columbia, Canada) and a MadgeTech® mini data logger (Warner, NH).

At the conclusion of the experiment (396 d), two vertically oriented samples were removed from the anaerobic chamber and exposed to air for 2 h. The samples were placed in individual containers of 500 ml of oxygenated and deoxygenated artificial seawater. The artificial seawater had been deaerated for 2 h with bubbling $N_2$ gas. $1/R_p - E_{corr}$ trends were recorded over an 8-d period, using a Ag/AgCl reference electrode and a carbon rod as a counter electrode.

Corrosion products were prepared for x-ray diffraction with an agate mortar and pestle under nitrogen, using acetone to prepare a slurry that was transferred to glass disks (2.54 cm diameter). A SCINTAG XDS 2000 X-ray diffractometer was used in the study. The instrument was operated at a voltage of 35 kV and 15 mA current. A step scan from 2 to 70° ($2\theta$) was used, 0.05° increment and 8 s dwell time per step. A steady stream of nitrogen was used to flood the interior of the instrument to prevent oxidation. Data were retrieved and converted to Excel spreadsheets by Diffraction Master.

## RESULTS

Changes in bulk water chemistry as a function of time for both exposure conditions are presented in Tables II (aerobic) and III (anaerobic). For the aerobic conditions, the pH decreased from 8.02 to 7.29 over the 396-d exposure. The initial pH in the anaerobic chamber was lowered to 6.23 because of $CO_2$ used in the deoxygenating process. The pH increased to 7.08 over the exposure period. In general, sulphide concentration in the bulk medium increased with time in both chambers. Bulk sulphide concentration in the anaerobic seawater was consistently higher

TABLE II The water chemistry of stagnant aerobic seawater

| Days Exposure | pH | Sulfide (ppm) | Sulfate (ppm) | Ammonia (ppm) | Nitrate/Nitrite (ppm) | Turbidity (NTU)* |
|---|---|---|---|---|---|---|
| 0 | 8.02 | < 0.01 | – | – | – | – |
| 60 | 7.33 | < 0.01 | 3812 | 0.88 | < 0.6 | 5.38 |
| 95 | 7.37 | 0.06 | 3856 | 0.56 | < 0.6 | 4.89 |
| 125 | 7.22 | 0.39 | 3360 | 0.79 | 1.0 | 3.8 |
| 152 | 7.25 | 0.40 | – | – | – | – |
| 181 | – | 0.30 | 3212 | 0.99 | < 0.6 | 2.34 |
| 220 | 7.23 | 0.31 | 3140 | 3.5 | < 0.0 | 1.58 |
| 258 | 7.23 | 0.13 | 3168 | 3.0 | < 0.6 | 1.34 |
| 312 | 7.25 | 0.20 | – | 1.97 | 0.7 | 1.41 |
| 396 | 7.29 | 0.30 | 2916 | 4.06 | < 0.6 | 8.01 |

* NTU = Nephelometric Turbidity Units

TABLE III The water chemistry of stagnant anaerobic seawater

| Days Exposure | pH | Sulfide (ppm) | Sulfate (ppm) | Ammonia (ppm) | Nitrate/Nitrite (ppm) | Turbidity (NTU) |
|---|---|---|---|---|---|---|
| 0 | 6.23 | < 0.01 | – | – | – | – |
| 48 | 6.79 | 0.52 | 3692 | < 0.2 | 3.1 | 6.39 |
| 83 | 6.72 | 0.74 | 3784 | < 0.2 | 0.8 | 27.4 |
| 113 | 6.91 | 0.49 | 3608 | < 0.2 | < 0.6 | 5.56 |
| 140 | 7.01 | 0.50 | – | – | – | – |
| 173 | 7.07 | 0.67 | 2948 | 0.3 | 0.8 | 53.9 |
| 208 | 6.92 | 0.41 | 2688 | 0.2 | 1.1 | 4.22 |
| 246 | 7.07 | 0.65 | 2900 | 0.2 | 1.6 | 25.5 |
| 302 | 7.09 | 0.53 | – | < 0.2 | 2.4 | 14.7 |
| 396 | 7.08 | 0.50 | 2024 | < 0.2 | < 0.6 | 40.8 |

than that of the aerobic seawater. Sulphate concentrations declined in both cases. Low concentrations of ammonia were measured in both exposure conditions. Turbidity consistently decreased with time in the aerobic water and fluctuated under anaerobic conditions. The microbial population of the bulk water varied with exposure condition. In the chamber maintained with exposure to air, all measured microbial populations (Table IV) initially decreased with time, but at the conclusion of the experiment (396 d) the populations of aerobes and anaerobes returned to their original numbers. Culturable SRB were observed at 60 d in the aerobic condition. Under anaerobic conditions (Table V) the numbers of culturable anaerobic bacteria *i.e.* general anaerobic heterotrophs, APB and SRB, increased with time. Populations of culturable SRB increased by five orders of magnitude over the entire experiment.

At the conclusion of the experiment, general observations were made of the condition of the water in each chamber. The bottom of the aerobic chamber was covered by large amounts of settled reddish/brown corrosion products, while the anaerobic chamber had black corrosion products at the bottom. The aerobic water had a stale smell, while the anaerobic water smelled of sulphide.

DO concentration (Figure 3) for the aerobic seawater fluctuated between 4 ppm (mg $l^{-1}$) and 1 ppm over the entire exposure period. The initial DO concentration of 4.3 ppm decreased to 1.6 ppm during the first 10 d and fluctuated over the next

TABLE IV The numbers and types of bacteria in aerobic seawater

| Exposure (days) | Aerobes $(10)^6$ | Anaerobes $(10)^6$ | APB $(10)^6$ | SRB $(10)^6$ |
|---|---|---|---|---|
| 0 | 4 | 3 | 4 | 0 |
| 60 | 1 | 1 | 1 | 1 |
| 259 | 2 | – | 1 | – |
| 396 | 4 | 3 | 1 | 0 |

TABLE V The numbers and types of bacteria in anaerobic seawater

| Exposure (days) | Aerobes $(10)^6$ | Anaerobes $(10)^6$ | APB $(10)^6$ | SRB (10) |
|---|---|---|---|---|
| 0 | 4 | 3 | 4 | 0 |
| 48 | 3 | 5 | 5 | 3 |
| 247 | 2 | 3 | 2 | 4 |
| 396 | 3 | 4 | 4 | 5 |

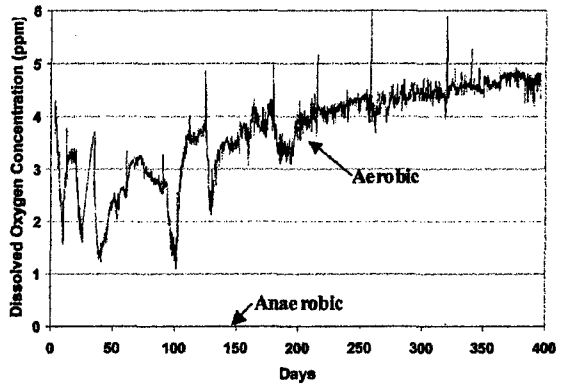


FIGURE 3 Dissolved oxygen concentration (ppm) over time for both aerobic and anaerobic stagnant conditions. Periodic upward spikes in the aerobic data indicate sample removal.

200 d. After 200 d, DO concentration increased slowly from 3.5 to 4.5 ppm. The oxygen-stripped seawater had an initial DO concentration of < 1 ppm and quickly dropped to 0 in the first days, and remained at 0 for the 396 d of exposure.

$E_{corr}$ was monitored continuously for each of the 1020 carbon steel electrodes over the entire exposure in both the aerobic and anaerobic chambers. Figure 4 shows the average $E_{corr}$ values by row for both aerobic and anaerobic cases. Standard deviations of average $E_{corr}$ values were 1% or lower throughout the entire experiment (not shown). The $E_{corr}$ values for all samples started at approximately −0.75 V (Ag/AgCl). Over the next 80 d, the $E_{corr}$ values for the aerobic condition increased by 40 mV. In contrast, the $E_{corr}$ values in the anaerobic chamber increased by 40 mV but at approximately 45 d the $E_{corr}$ values of the different orientations (vertical, rows 1–3 and horizontal, row 4) separated. The $E_{corr}$ of row 4 coupons decreased to approximately −0.74 V (Ag/AgCl) in a few days and then slowly increased by

20 mV over the next 50 d. The $E_{corr}$ of the vertical rows decreased to −0.74 V (Ag/AgCl) over 20 d, but in contrast to row 4 did not increase after dropping to −0.75 V (Ag/AgCl). The quick drop and separation of the $E_{corr}$ values at 45 d corresponded to an increase in sulphide concentration (Table III) and culturable SRB (Table V). A notable difference between exposure conditions throughout the entire experiment was the observation of small fluctuations ($\pm$ 5 mV) of the $E_{corr}$ values in the aerobic condition while the $E_{corr}$ values for coupons in the anaerobic chamber remained stable. At 80 d in the aerobic condition, the fluctuations began to increase to almost 100 mV in amplitude. At day 87, the datalogger malfunctioned and data were lost until day 115 at which time the fluctuations increased to approximately 200 mV in amplitude. Fluctuations continued until day 200 of exposure at which time the $E_{corr}$ values stabilized. Small fluctuations were still apparent. The $E_{corr}$ rose by 50 mV over the remainder of the experiment. Stabilization of the $E_{corr}$ and DO occurred at same time *i.e.* day 200. No appreciable difference in $E_{corr}$ was observed between the coupons as a function of row in the aerobic case. In the case of the anaerobic exposure, between 60 and 110 d the horizontal (bottom, row 4) coupon $E_{corr}$ began to increase to almost −0.71 V (Ag/AgCl) while the vertical (side, rows 1, 2 and 3) coupons $E_{corr}$ remained at −0.74 V. Simultaneously, a stratification of $E_{corr}$ values was observed between the two orientations (horizontal and vertical) in the anaerobic case. At approximately day 150, the $E_{corr}$ of row 1 separated from rows 2 and 3, both of which slowly decreased by 20 mV over the next 50 d. At day 200, the $E_{corr}$ of rows 2 and 3 separated also. Jumps in the $E_{corr}$ at days 260 and 305 indicated disturbances due to sample collection. After 305 d, all the $E_{corr}$ value for coupons in the anaerobic chamber had begun to merge to a single value around −0.72 V (Ag/AgCl).

Linear polarization measurements were performed on individual electrodes in both exposure conditions over the 396-d exposure. $R_p$ was calculated for each sample and $R_p$ values were averaged by row and exposure type. Standard deviations of average instantaneous corrosion rates were 9% or less for the

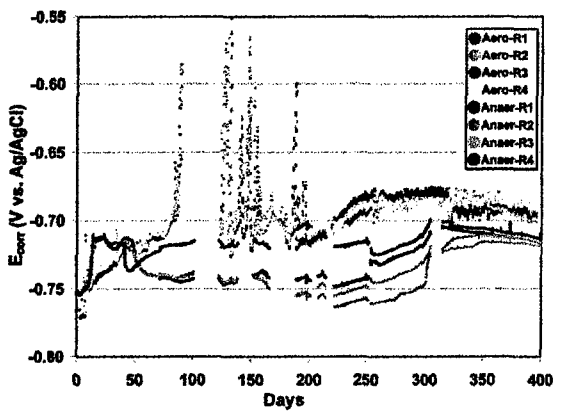


FIGURE 4 Average $E_{corr}$ (*vs* Ag/AgCl) over time values for C1020 samples in stagnant aerobic (aero) and anaerobic (anaer) conditions displayed by row (R). R1, R2, R3 = vertically orientated samples with R1 being at the top of the tank, R3 towards the bottom and R2 between the two; R4 = horizontally orientated sample at the bottom of the tank.

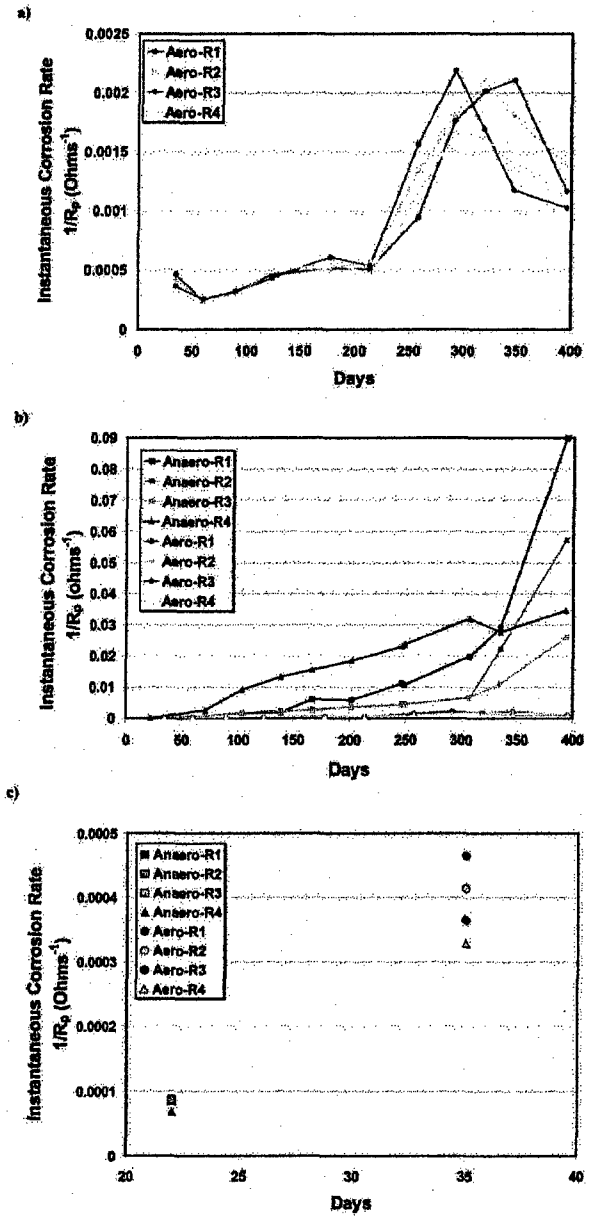


FIGURE 5 $1/R_p$ (instantaneous corrosion rate) over time (days) for C1020 samples in stagnant (a and b) aerobic and (b) anaerobic conditions. Aerobic conditions are included with anaerobic data (b) to indicate the much higher rates in anaerobic conditions. Early corrosion rates are shown in (c) for both aerobic and anaerobic conditions. R1, R2, R3 = vertically orientated samples with R1 being at the top of the tank, R3 towards the bottom and R2 between the two; R4 = horizontally orientated sample at the bottom of the tank. Average values are displayed.

aerobic condition, while the anaerobic condition had higher standard deviations of 18% or less throughout the entire experiment. The inverse, $1/R_p$ (a value proportional to the instantaneous corrosion rate) was plotted *vs* exposure time (Figure 5a, 5b). Standard deviation bars are not shown in Figure 5 to preserve data clarity. Between 23- and 35-days exposure, the corrosion rates for all samples were relatively low with the lowest being the anaerobic case (Figure 5c). Corrosion rates are reported in $ohms^{-1}$; these data were not normalized to the 2 $cm^2$ electrode area. At the same time, $1/R_p$ values indicated stratification within the aerobic chamber. Row 1 electrodes, closest to the air/water interface, had the highest average corrosion rate, while row 4 electrodes had the lowest. No indications of stratification were observed in the anaerobic chamber in the early exposure times. After > 100 d exposure, the $1/R_p$ measurements indicated that the highest instantaneous corrosion rate was measured in the horizontal (bottom, row 4) coupons exposed to anaerobic seawater. This separation of bottom and side coupon corrosion rate after 23 d corresponds to the separation of $E_{corr}$ at approximately the same time. At 200 d in the aerobic condition, the corrosion rate increased for all rows, corresponding to the stabilization of $E_{corr}$. In the anaerobic case, the corrosion rate of row 1 separated and increased from rows 2 and 3 (corresponding to an increase in the $E_{corr}$). After 300 d, the corrosion rate of row 2 separated from row 3 and increased. Figure 5b has both anaerobic and aerobic corrosion rates plotted to facilitate the direct comparison of the instantaneous

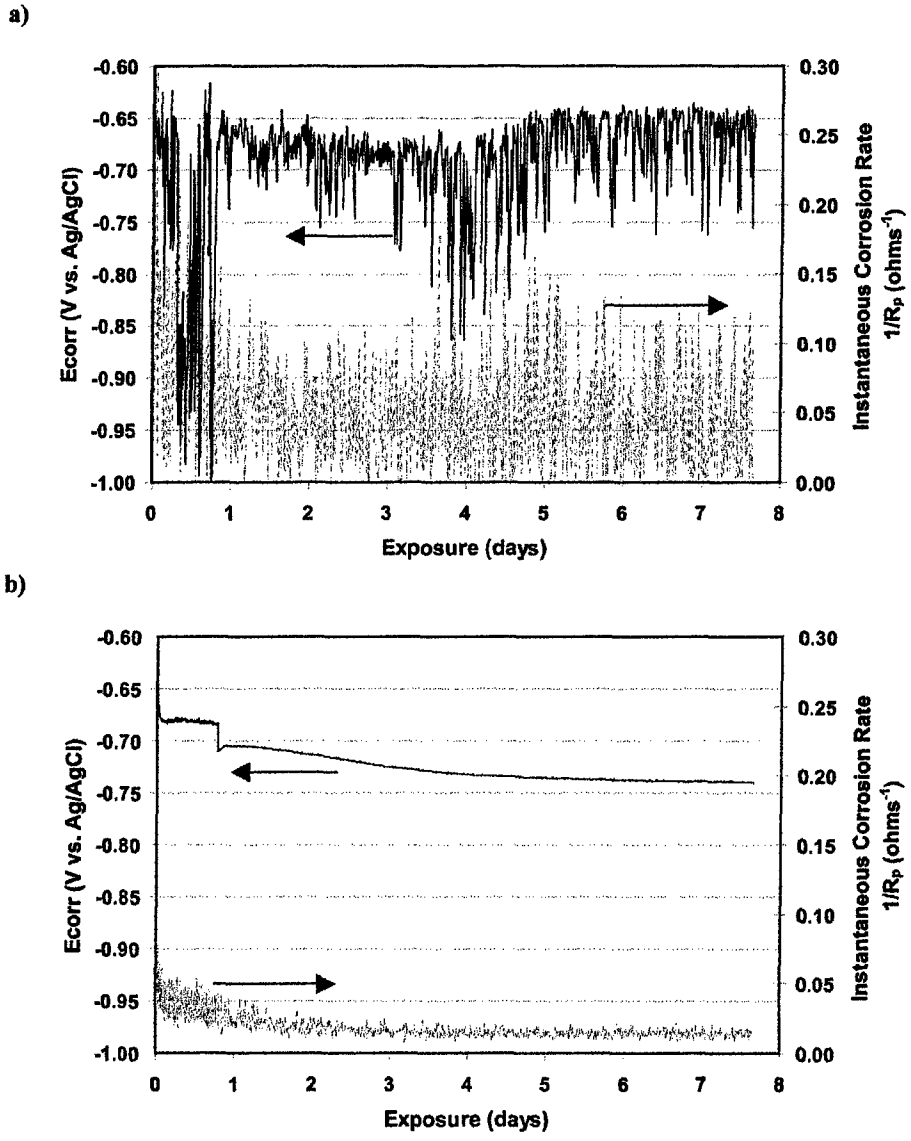


FIGURE 6 $1/R_p - E_{corr}$ trend of anaerobic samples previously exposed to anaerobic conditions for 396 d, exposed to air for 2 h, and placed in (a) aerated artificial seawater and (b) deaerated artificial seawater.

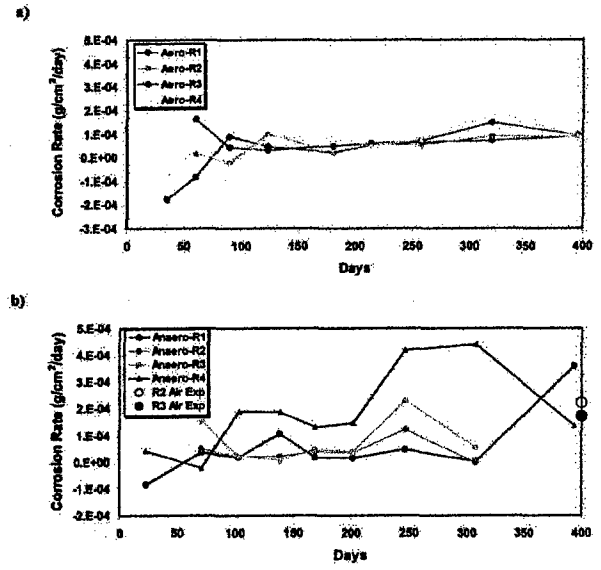


FIGURE 7 Corrosion rate (g $cm^{-2}$ $d^{-1}$) from weight loss data over time (d) of C1020 samples in stagnant (a) aerobic and (b) anaerobic conditions. R1, R2, R3 = vertically orientated samples with R1 being at the top of the tank, R3 towards the bottom and R2 between the two; R4 = horizontally orientated sample at the bottom of the tank. In the anaerobic condition (b), after 394 d exposure, samples removed from R2 (○) and R3 (●) were exposed to air for 2 h. The R2 sample was placed in stagnant aerated seawater and the R3 sample was placed back in the anaerobic tank for 8 d, removed, cleaned and weighed.

corrosion rates. In general, instantaneous corrosion rates for the anaerobic condition were two orders of magnitude higher than the aerobic condition.

The $E_{corr}$ values for the two samples removed from the anaerobic chamber, exposed to air for 2 h, and placed in containers of aerated and deaerated artificial seawater are presented in Figure 6a and b, respectively. In aerated seawater, values fluctuated between −0.6 V and −1.0 V (Ag/AgCl). The largest fluctuations occurred in the first day of exposure. The $1/R_p$ data also fluctuated, with the largest fluctuations measured in the first day of exposure. In contrast, the sample exposed to deaerated seawater displayed stable $1/R_p$ and $E_{corr}$ (Figure 6b).

Corrosion rates (gm $cm^{-2}$ $d^{-1}$) derived from weight loss data were not a function of sample orientation in the aerobic condition. As indicated in Figure 7a, weight loss corrosion rate in the aerobic condition generally increased slightly over time. Initially, some weight gain was observed. This seeming contradiction is directly attributed to the acid-resistant corrosion product. For the first 146 d of the experiment, the weight of the tenacious iron oxide varied from 2.1 mg to 2.9 mg (weight loss due to caustic cleaning). After 146 d the weight of the tenacious layer was 0.4 mg or less. Weight loss corrosion rate for coupons exposed in anaerobic conditions is displayed in Figure 7b. No distinction in corrosion rate over time can be made between the vertically orientated samples (rows 1, 2, and 3). In general, the horizontally orientated samples had the largest corrosion rate in the anaerobic condition until 396 d exposure at which time row 1 had a significant increase in corrosion rate; while row 4 showed a decrease. This change is also seen in the $1/R_p$ data (Figure 5b). Figure 7b also indicates the weight loss corrosion rate of the two samples which were exposed to air and then returned to aerated (row 2) or deaerated seawater (row 3). The weight loss was greater for the aerobic exposure than the anaerobic exposure. Both samples had less weight loss than row 1, but more than row 4 at the end of the experiment.

The appearance of the electrodes varied with exposure condition. Observations have been documented in Figures 8 and 9. The corrosion products that formed under aerobic and anaerobic seawater conditions were predictably different in appearance and composition. Under aerobic conditions, reddish brown corrosion products, identified as lepidocrocite and goethite by XRD, persisted on the surfaces of all coupons/orientations throughout the experiment (Figure 8a, b). Filamentous bacteria were associated with the oxides (Figure 8c, d), but were obscured by the oxides by the conclusion of the experiment (Figure 8e, f). The oxides were extremely tenacious and resistant to acid cleaning. The corrosion was general. Coupons exposed in anaerobic seawater were covered with black corrosion products (Figure 9a, b). Sulphur deficient iron sulphide (mackinawite) was identified in corrosion products within the first month of anaerobic seawater exposure. In later exposures, small amounts of pyrrhotite were identified in the corrosion products formed under anaerobic conditions. After day 139 the epoxy was blackened obscuring the coupons. The most conspicuous microorganisms in the sulphide corrosion products were curved rods (Figure 9c, d). The corrosion on the vertically oriented coupons was localized, deep gouging (Figure 9e) while the horizontally oriented coupon had a porous appearance with some deep pitting (Figure 9f). Pit depths were not measured.

## DISCUSSION

Previous investigators demonstrated that corrosion due to the activities of SRB is more aggressive in the presence of oxygen, *i.e.* corrosion of mild steel by SRB under completely anaerobic conditions was negligible compared to the corrosion of mild steel by SRB in the presence of oxygen. The experiments described in this paper were directed at answering a different question: Is oxygen required for the corrosion of mild steel in natural seawater?

Several investigators (Eashwar & Subramian, 1990; Mansfeld & Little, 1992; Lee *et al.*, 1993a; 1993b) have demonstrated that natural marine

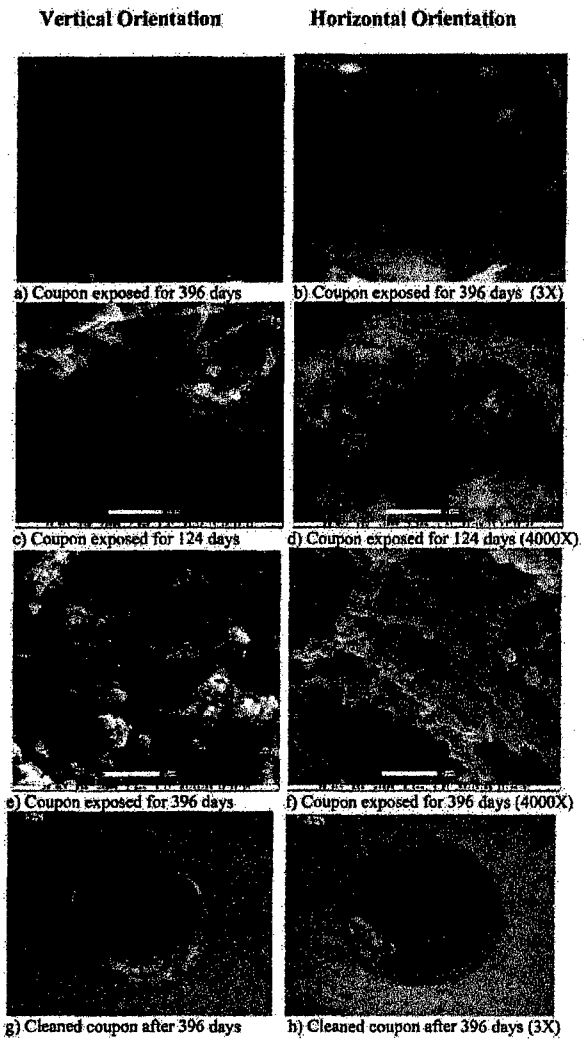


FIGURE 8 Photographs and micrographs of C1020 samples exposed to stagnant aerobic natural seawater.

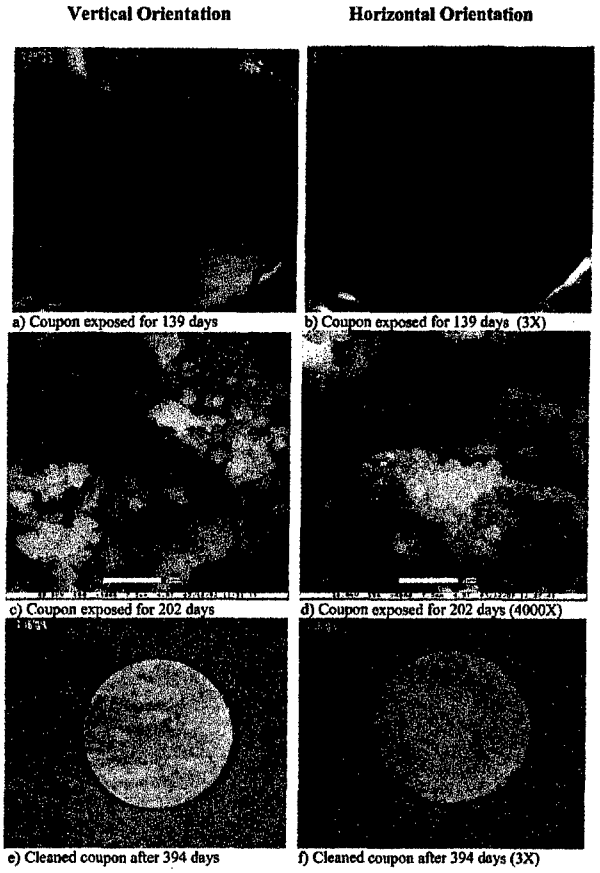


FIGURE 9 Photographs and micrographs of C1020 samples exposed to stagnant anaerobic natural seawater.

biofilms form on metal surfaces, providing an anaerobic metal/biofilm interface and an environment for the growth of SRB, independent of bulk oxygen concentrations. Biofilms 75 $\mu$m thick in aerobic media can produce anaerobic conditions at the biofilm/metal interface if the aerobic respiration rate is greater than the diffusion rate of oxygen into the biofilm (Lee *et al.*, 1993a; 1993b; Lee *et al.*, 1995). Hamilton and his co-workers (Sanders & Hamilton, 1985; Hamilton, 1999, 2000; Hamilton & Lee, 1995) were the first to demonstrate sulphide production by SRB within anaerobic niches of biofilms in oxygenated seawater. Despite this possibility, there were no indications of anaerobic niches and sulphide production within the oxide corrosion layers formed under the aerobic experimental conditions described in the present paper. The EDS and XRD spectra indicated iron oxides with traces of phosphorus and calcium. No sulphur could be detected by EDS in the corrosion products over the 396-d exposure period, indicating the absence of sulphide corrosion products. XRD confirmed the presence of iron oxides, lepidocrocite and goethite. After acid cleaning, an adherent layer of black iron oxide remained on the surface of the coupons exposed to aerobic seawater. Removal required caustic cleaning.

Most of the previous laboratory experiments on SRB-induced corrosion of carbon steels exposed to seawater were conducted with nutrient-supplemented artificial seawater and an inoculum of 1 – 3 microbial species. Nutrients can influence the experimental outcome in several ways. Attachment of cells to surfaces is a strategy for bacterial survival in environments where the bulk water phase is nutrient limiting. Geesey (1987) stressed that many survival mechanisms are not expressed when microorganisms are subjected to the laboratory conditions used for most microbiological research.

Hydroxide, acetate and carbonate can inhibit pitting corrosion by acting as buffers. Oxyanions (*e.g.* $SO_4^{2-}$, $NO_3^-$, $PO_4^{3-}$ ) are often present in nutrients. Molar $Cl^-$/oxyanion ratios can be used to predict the likelihood of pitting or crevice corrosion (Leckie & Uhlig, 1966; Kehler *et al.*, 2001). The

relationships between the concentration of inhibitive and aggressive anions correspond to competitive uptake of the anions by adsorption or ion exchange at a fixed number of sites on a metal surface. Webster and Newman (1994) examined the impact of media constituents on localized corrosion and concluded that $Cl^-$ must be present in a concentration at least comparable to that of all other anions combined, otherwise corrosion was inhibited even at high $H_2S$ concentrations (up to 500 ppm). Other corrosion investigators have concluded that extra nutrients cannot be added to stimulate bacterial growth and MIC if those nutrients inhibit corrosion by adding too many non-chloride ions (Ringas & Robinson, 1988). Clearly, the electrolytes in the Hardy and Bown (1984) and Lee (1993a; 1993b) experiments contained enough $Cl^-$ to sustain localized corrosion. However, any reduction of the ratio of $Cl^-$ to other inhibiting anions can increase the time to initiation and decrease the propagation rate of localized corrosion (Webster & Newman, 1994).

Additionally, Webster and Newman (1994) observed interferences in electrochemical measurements when yeast extract was included in the culture medium/electrolyte. The interferences were removed when the yeast extract was removed. Both Hardy and Bown (1984) and Lee *et al.* (1993a; 1993b) used nutrient-enhanced media that contained yeast extract (500 mg $l^{-1}$ and 10 mg $l^{-1}$, respectively) in their laboratory studies.

The experiments described in the present paper demonstrate that corrosion of carbon steel was more aggressive under totally anaerobic conditions as compared to exposures in oxygenated seawater. In these experiments, oxygen concentration in both exposure tanks decreased within the first hours/days of the exposure period due to aerobic respiration and corrosion reactions. Lee *et al.* (1993a; 1993b) observed a decrease in DO concentration in the bulk from 1.5 ppm to 0.4 ppm within the first 20 d of exposure that they attributed to cell respiration. Corrosion was more severe on the horizontally oriented samples than on the vertically oriented coupons in both exposure conditions. Bacteria were located within the corrosion products formed under aerobic and anaerobic conditions. The most conspicuous organisms in the corrosion products formed under aerobic conditions were filaments, often twisted and encrusted with iron oxides. Corrosion of the carbon steel exposed under completely aerobic conditions did not appear to be influenced by the presence of the bacteria in the corrosion products. Under anaerobic conditions the most conspicuous organisms were short curved rods encrusted with iron sulphides. The corrosion of the carbon steel exposed under totally anaerobic conditions was typical of microbiologically influenced corrosion by SRB.

Zintel and Kostuck (2002) evaluated corrosion and corrosion mitigation for carbon steel exposed to stagnant Gulf of Mexico seawater for 3 months. Mitigation strategies included oxygen scavengers, biocides and/or filtrations. All coupons had some uniform corrosion. The deepest pits, 54 $\mu$m and 28 $\mu$m, were observed on coupons exposed to natural seawater or filtered seawater (20 $\mu$m pore size, followed by 5 $\mu$m pore size, followed by 0.2 $\mu$m pore size) to which an oxygen scavenger, ammonium bisulphite ($NH_4HSO_3$), was added. The deepest pit was measured in the natural deoxygenated seawater.

In the present experiment, under totally anaerobic natural seawater conditions, mackinawite, a sulphur deficient iron sulphide, $FeS_{(1-x)}$, formed on the carbon steel coupons. In the last months of exposure the mackinawite was converted to pyrrhotite, $Fe_{(1-x)}S$, a sulphur rich iron sulphide indicating a higher reduced state of iron. In some cases the corrosion products contained 30% sulphur, in addition to phosphorus and iron. The concentration of sulphur is especially high when taking into account the bulk water sulphide was $< 1$ ppm throughout the experiment (Table III). A similar observation was made by Lee *et al.* (2003) with 70Ni/30Cu exposed to artificial seawater inoculated with SRB. MIC of mild steel by SRB has been reviewed extensively (Sanders & Hamilton, 1984; Hamilton & Lee, 1995; Lee *et al.*, 1995; Lewandowski *et al.*, 1997; Nielsen *et al.*, 1993; Hamilton, 1999, 2000). SRB within mixed species biofilms produce sulphide that reacts with iron to produce iron sulphide corrosion products that may be either protective or corrosive. King and Wakerly (1973) demonstrated that the initial sulphide film that forms in the presence of SRB is mackinawite. They further demonstrated that sulphides moderate, but do not prevent corrosion. When iron sulphides form a tightly adherent thin film, they are protective. However, iron sulphides are inherently unstable and their disruption can give rise to corrosion cells between the iron sulphide in direct electrical contact with the underlying steel (cathode) and the exposed-steel surface (anode). In their experiments, continued availability of sulphide leads to a steady thickening of the sulphide layer and a transformation of mackinawite to greigite, $Fe_3S_4$ and eventually to pyrrhotite. Transformation between sulphide species depends on pH, temperature, redox potential and relative concentration of reactants. King and Wakerly (1973) determined that each sulphide had a characteristic corrosiveness but the attack was consistently pitting.

Carbon and energy flux in both individual cells and microbial ecosystem require electron transfer and metal ion oxidation/reduction. In his 'unifying electron transfer hypothesis,' Hamilton (2003) concluded that the activities of microorganisms produced kinetically favoured pathways of electron flow from the metal anode to the universal electron

acceptor, oxygen. He observed that microbial ecosystems, including soils, sediments, water columns, and biofilms, are characterized by aerobic and anaerobic zones that operate as a continuum via redox couples within the ecosystem. The interactions between oxygen and sulphate depend on redox cycling via intermediate electron carriers. The present authors observed evidence of stratification in the aerobic chamber in terms of $E_{corr}$ within 23 d (Figure 5c). Hamilton (2003) further stressed that biofilm growth is a dynamic process and the microorganisms within the biofilm are in a constant state of flux. Individual bacterial species and bacterial consortia are characterized by their primary energy source and electron donor and by the nature of the terminal electron acceptor. Oxygen is the terminal electron acceptor for aerobic species, but for anaerobic species there are alternate electron acceptors, *e.g.* nitrate, sulphate, ferric iron, and $CO_2$. It is possible that in the complex chemistry of seawater and biofilms there are electron acceptors other than oxygen to drive electron transfer and drive corrosion reactions. Under the experimental conditions described in this paper, corrosion of carbon steel was more aggressive in totally anaerobic conditions than in aerobic conditions. On-going experiments have been designed to evaluate the impact of alternating aerobic/anaerobic conditions in more rigorous experimental conditions.

## CONCLUSIONS

In the experiments described in this paper, coupons exposed to natural aerobic seawater for 396 d developed intact, tenacious iron oxide surface deposits. In contrast, the coupons exposed anaerobically over the same period were covered with non-tenacious sulphides. Anaerobic conditions did not inhibit corrosion and oxygen was not required for aggressive localized corrosion. Once oxygen was introduced to a carbon steel coupon previously maintained under strictly anaerobic conditions, the corrosion was extremely aggressive.

### *Acknowledgements*

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